

Aggregation of Starburst™ (PAMAM) Dendrimers on the Surface of Bare and Thiol Modified Gold Substrates

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Abstract

The preparation and characterization of surface modified substrates, has been the subject of a substantial research effort during the last two decades¹. Among the many techniques reported for the synthesis of modified surfaces, the covalent attachment of thiolated species to the surface of clean gold substrates has proved to be one of the easiest and most reliable approaches developed so far². On the other hand, since their invention about twenty years ago, the dendrimers, also known as cascade or hyper-ramified polymers, have captured the interest and fascination of many research groups around the world³. Although the number of recent publications in the scientific literature clearly reveal this fact, most of the work has been focused on the development of synthetic protocols and therefore has been carried out in solution. The use of dendrimers to modify the structure, properties and behavior of surfaces, and in particular of electrochemical interfaces, is therefore a research field that has been barely explored⁴. In this work, we report the results on a study that is aimed to understand the factors that control the aggregation of commercial Starburst PAMAM dendrimers on the surface of bare and thiol modified gold electrodes from aqueous neutral solutions. In particular, we have studied the aggregation of two similar Starburst PAMAM dendrimers (each one bearing either 64 carboxylic acid or amine peripheric functional groups), on the surface of bare and modified substrates characterized by submonolayer coverages of either carboxylic ($\text{HS}(\text{CH}_2)_2\text{COOH}$) or amine terminated ($\text{HS}(\text{CH}_2)_2\text{NH}_2\text{Cl}$) thiols. The aggregation of these polymeric materials from μM solutions of dendrimers on the surface of bare and modified gold electrodes was followed using QCM measurements and, as expected, the complementary electrostatic interaction between opposite charged species was found to promote much larger dendrimer coverages for thiol modified electrodes than those found for clean gold substrates. Computer fitting of the aggregation QCM curves to a Frumkin isotherm model⁵, revealed that the main effect of the presence of the short thiol on the surface of the gold electrode is not an increased energy of adsorption (consequence of electrostatic interactions) but a decrease on the lateral repulsive interactions between the dendrimer molecules. In this way, whereas the aggregation of both dendrimers on the surface of clean gold substrates achieve a surface coverage between 40-45 % of a dense monolayer at a dendrimer concentration of 15 μM , the fraction of covered surface on thiol modified gold electrodes is close to 90% at the same dendrimer concentration.

In a second stage of the work, we decided to study the effect that the aggregated dendritic polymers have on the electrochemical behavior of reversible electroactive species that are either neutral or densely charged. Therefore, using either bare and thiol modified gold electrodes, we monitored the electrochemical response of $\text{Ru}(\text{NH}_3)_3^{2+}$, $\text{Fe}(\text{CN})_6^{3-}$ and ferrocene solutions at different concentrations of the two dendrimers under study. Our results show that as the concentration of dendrimer is increased, the electroactive species of the same charge of the dendritic polymer exhibit an interfacial pre-concentration effect reflected by an important increase of the observed current density. Neutral electroactive species as well as those characterized by an electric charge of the same nature as that of the added dendrimer, show on the other hand a decrease on the observed current density that we postulate is a consequence of a blocking effect. Additional experiments aimed to determine the nature and structure of the complexes

presumably formed between the PAMAM dendrimers and the electroactive species considered in this study are currently being carried out in our laboratory.

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